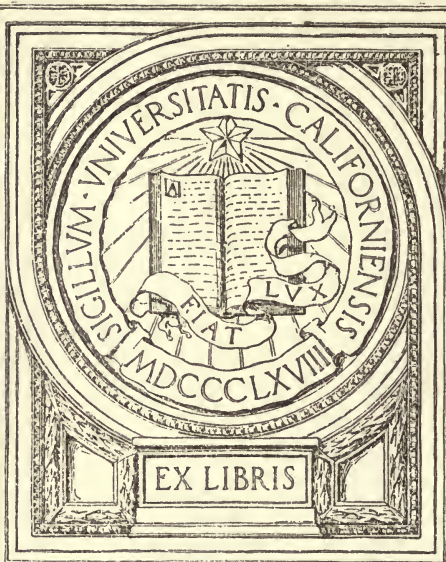


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# Are Electrolytes Completely Ionized at Infinite Dilution?

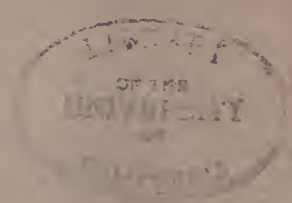
FEB 19

## DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the  
Degree of Doctor of Philosophy in the Faculty  
of Pure Science, Columbia University  
in the City of New York.

BY

Harold E. Robertson, A. B.



NEW YORK CITY

1921

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EXCHANGE

TO  
MY FATHER AND MOTHER

#### ACKNOWLEDGMENT

It is with great pleasure that I express my sincere appreciation of the constant advice and assistance of Professor Harold A. Fales under whose direction this work was carried to completion.



## ARE ELECTROLYTES COMPLETELY IONIZED AT INFINITE DILUTION?

Ever since the acceptance of the ionic theory put forward by Arrhenius<sup>1</sup> one of the most fundamental questions has been the degree of ionization of electrolytes at infinite dilution. The idea generally held at present, as a result of extensive investigations by means of conductivity measurements, is that as we approach infinite dilution, the degree of ionization approaches unity.

However there are several objections to the conclusions which have been drawn from conductivity data. These objections have partly to do with the measurements themselves, and partly with their interpretation. With respect to the former we may mention principally that it is not practicable without using apparatus of extreme complexity<sup>2</sup> to make measurements at dilutions<sup>3</sup> in excess of one thousand liters per mol because of the relatively enormous errors which are introduced by the presence of the merest traces of impurities in the solution being measured; with respect to the latter we may mention, first the uncertainty which exists as to the water correction which must be applied, and, secondly the fact that the value of the equivalent conductivity at infinite dilution  $\Lambda_0$ <sup>4</sup>, is obtained not by direct experiment but by extrapolation from measurements of  $\Lambda$  stopping at the lower limit of  $\Lambda_{0.001}$ . Among the numerous formulae for making this extrapolation the ones which have been employed most frequently are those due to Kohlrausch<sup>5</sup>, Noyes<sup>6</sup>, Storch<sup>7</sup>, Kraus and Bray<sup>8</sup>, Kendall<sup>9</sup>, and Washburn<sup>10</sup>. A complete discussion of the various methods of calculation and the errors incident thereto is given by Bates<sup>11</sup>.

<sup>1</sup> Z. Physik. Chem. 1, 631 (1899).

<sup>2</sup> Washburn, J. Amer. Chem. Soc. 40, 122 (1918).

<sup>3</sup> The term dilution as used here means the number of liters of solution containing one mol of solute.

<sup>4</sup> This is also called  $\Lambda_{00}$ .

<sup>5</sup> Wiss. Abh. Phys. Tech. Reichanstalt. 3, 155 (1900).

Sitzunber, konigl. preuss. Akad. (1900).

Z. Elektrochem. 13, 333 (1907).

<sup>6</sup> Pub. Car. Inst. 63, 337 (1907).

<sup>7</sup> Z. Physik. Chem. 19, 13 (1896).

Bancroft, *ibid.*, 31, 188 (1899).

<sup>8</sup> J. Amer. Chem. Soc. 35, 1315 (1915).

<sup>9</sup> Trans. Chem. Soc., 101, 1275 (1912).

<sup>10</sup> *loc. cit.*

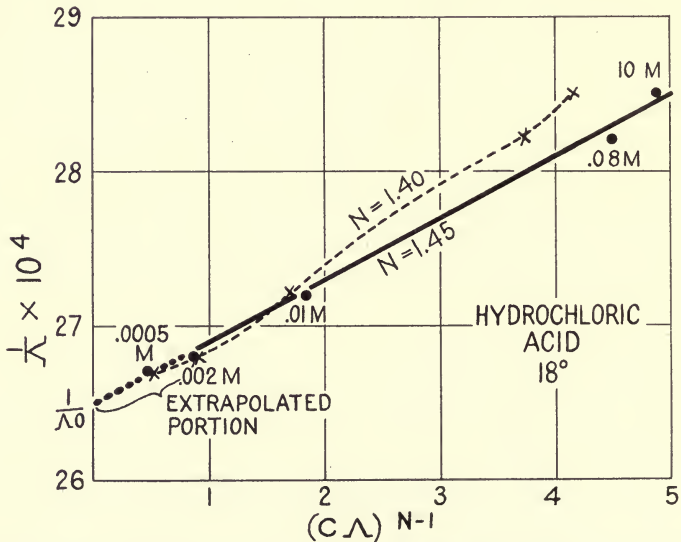
<sup>11</sup> J. Amer. Chem. Soc. 35, 519 (1913).

The curve given below in Fig. I illustrates the method followed by Noyes<sup>1</sup> in determining  $\Lambda_0$ . The equation used by this author is:  $\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + K(C\Lambda)^{n-1}$ ,  $\frac{1}{\Lambda}$  being plotted against  $(C\Lambda)^{n-1}$  and  $n$  being varied until the nearest approach to a straight line is obtained. The dotted portion of the curve shows the extrapolation for  $n = 1.45$ . The data is taken from the section of Noyes' work on hydrochloric acid at 18°; it is (Table I):

TABLE I

Conc. HCl.	$\frac{1}{\Lambda} \times 10^4$	$(C\Lambda)^{n-1}$ ( $n = 1.45$ )	$(C\Lambda)^{n-1}$ ( $n = 1.40$ )
0.0005 M	26.7	0.47	0.50
.002	26.8	0.857	0.89
.01	27.2	1.84	1.69
.08	28.2	4.50	3.73
.10	28.5	4.84	4.15

FIG I



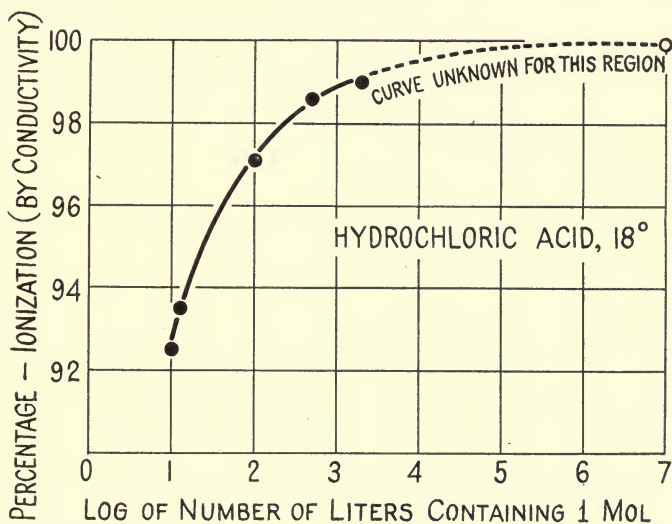
Putting this same data in somewhat different form and plotting degree of ionization against the logarithm of dilution in order to show the assumed approach to complete ionization with increasing dilution as extrapolated from conductivity measurements we get the data of Table II and the curve given in Fig II.

<sup>1</sup> loc. cit.

TABLE II

Conc. HCl.	Log. of Dilution	Percentage Ionization
0.1	1.0	92.5
0.08	1.1	93.5
0.01	2.0	97.1
0.002	2.7	98.6
0.0005	3.3	99.0

FIG. II



In view of the preceding considerations it would seem highly desirable to bring to bear some independent method of investigation in regard to the behavior of the ionization of electrolytes in the region under discussion. Such a method seems to be present in the electromotive method of Nernst<sup>1</sup> for the measurement of ionic concentrations, and it may be pertinently mentioned here that this method for the region under consideration is free from the experimental difficulties which seem to render the conductivity method of slight, if any, avail; thus the presence of slight impurities derived by the solutions either from their containing vessels or the air have no appreciable effect on the e.m.f. measurements, and further the enormous specific resistance of the solutions being measured is no obstacle if the ballistic galvanometer is employed in place of the potentiometer according to the method described by Beans and Oakes<sup>2</sup>.

<sup>1</sup> Z. Physik. Chem. 4, 129 (1889).

<sup>2</sup> J. Amer. Chem. Soc. 42, 2116 (1920).

Because of the large amount of work that has been done on acids it was thought well by the present author to investigate the several types of acids: monobasic, dibasic, and tribasic, and accordingly hydrochloric, acetic, sulfuric and phosphoric acid solutions were made up in dilutions ranging from ten liters per mol to three million liters per mol. The concentration of hydrogen ion was calculated from the e.m.f. measurements

by means of Nernst's formula  $e = .000198 T \log \frac{C_{H^+}}{K\sqrt{pH_2}}$ .<sup>1</sup> The value

so obtained for  $C_{H^+}$  was multiplied by one hundred and divided by the total concentration of acid present times the valence of the anion. The quotient of this division is what we will call the thermodynamic percentage ionization.<sup>2</sup> The surprising fact is that the values so obtained rise generally to a maximum and then fall off rapidly toward zero as the dilution increases, cf. Fig. IV.

## EXPERIMENTAL METHOD

### Water Bath

To prevent electrical leaks the cells were immersed in an oil bath which was placed in a large water bath electrically regulated to  $25^\circ C \pm 0.01^\circ$ .

### Cells

The following e.m.f. combination was employed:

Hg—HgCl sat. KCl — sat. KCl — Hx — Hx —  $H_2$  (1 atmos.) Pt.<sup>3</sup>  
The saturated calomel cell as described by Fales and Mudge<sup>4</sup> was used throughout this work, likewise the hydrogen cells, electrodes and purifying train for the hydrogen. The hydrogen cells were steamed out before each series of determinations and the electrodes were also thoroughly boiled with distilled water. To determine whether the dissolving of materials from the hydrogen electrode cells would be appreciable, some conductivity and e.m.f. measurements were simultaneously taken. The

<sup>1</sup> In this formula, "e" represents the pole potential  $2C_{H^+}$  in volts, "T" = absolute temperature, logarithms are to the base 10,  $C_{H^+}$  is in mols per liter, "K" is the solution tension constant,  $pH_2$  is the partial pressure of the hydrogen in atmospheres.

<sup>2</sup> It seems desirable to follow the lead of M. C. McC. Lewis, Proc. Chem. Soc. 117, 1120 (1920) and call the hydrogen ion concentration as calculated from e.m.f. measurements by Nernst's formula the thermodynamic concentration of hydrogen ion, hence by a simple extension of this term we deduce the term "thermodynamic ionization." This is what G. N. Lewis, J. Amer. Chem. Soc. 35, 1 (1913), calls the activity of the hydrogen ion.

<sup>3</sup> The symbol Hx represents the acid being used.

<sup>4</sup> J. Amer. Chem. Soc. 42, 2434 (1920).

solution measured was 0.0000005 M. sulfuric acid. The fresh solution was placed in the hydrogen cell and the hydrogen passed for varying lengths of time with the results given in

TABLE III

Time	Specific Conductivity mhos.	Observed e.m.f. volt
0	$2.12 \times 10^{-6}$	.6352
1½ hr.	$4.08 \times 10^{-6}$	.6352
2½ hr.	$4.11 \times 10^{-6}$	.6352
2 weeks	$1.56 \times 10^{-5}$	.6350

It would seem from this that the effect of dissolving any impurities from the cells may be considered negligible, especially as the voltage was constant and reproducible regardless of the time that the solution was in the cell.

### Liquid Junctions

Reproducible results were obtained by using cotton plugs.<sup>1</sup> To prevent contamination of the solution being measured a double salt bridge was used. One beaker contained saturated potassium chloride into which calomel cell dipped. The other beaker contained the solution being measured and the goose-neck siphon hydrogen cell dipped into this. Connection between the two beakers was made by a siphon tube of internal diameter of about 0.5 cm., plugged with cotton wool and containing the solution being measured. This method gave very constant and reproducible results, the voltage of the system remaining practically constant for several hours after the solution and electrode had become saturated with hydrogen.

### Preparation of Materials and Solutions

Conductivity water was used in making up the solutions, as used, the water had a specific conductivity at 25° of about  $1.7 \times 10^{-6}$  mhos.; its content of ammonia was 0.5 mg. ( $3 \times 10^{-8}$  mol) of  $\text{NH}_3$  per liter<sup>2</sup>; when tested electrometrically in combination (I) at sundry times, the observed voltages for the portions tested lay between 0.660 and 0.680 volt. The mercury used in the calomel cells was purified by washing several

<sup>1</sup> Fales and Mudge, loc. cit.

<sup>2</sup> Whether this ammonia is present as ammonium hydroxide or some ammonium salt is a question which can not be settled experimentally. Judging from the work of Kendall, J. Amer. Chem. Soc. **38**, 1480 (1916), who offers evidence to show that conductivity water in contact with the air has a content of  $\text{CO}_2$  of  $1.4 \times 10^{-5}$  mols per liter and from the work of Paine and Evans, Proc. Camb. Phil. Soc., (1) **18**, 1 (1914), on the conductivity of dilute solutions of sulfuric acid containing very small amounts of ammonium carbonate, it would seem a reasonable premise that the ammonia is present as ammonium carbonate.



times in nitric acid by the method of Hildebrand<sup>1</sup>, filtering through a dry, clean towel and distilling under reduced pressure according to the method of Hulett.<sup>2</sup>

The potassium chloride used in the cells was a c.p. analyzed sample, twice recrystallized from water and then fused in platinum. For the salt bridge the analyzed sample was used without purifying. The calomel for the cells was a c.p. analyzed sample of such grade as had been found by Fales and Mudge<sup>3</sup> to give satisfactory results. The hydrochloric acid was purified by diluting a 12 molar solution of a c.p. analyzed sample with an equal volume of water, distilling and collecting the middle portion. The acetic, sulfuric and phosphoric acids were c.p. analyzed materials used as obtained. All solutions were made up at 25°. The hydrochloric and acetic acids were each made up to a concentration of 0.1 M., the sulfuric acid 0.05 M., and the phosphoric 0.0333 M.<sup>4</sup>; these stock solutions were kept in "Non-Sol" bottles, which had been well steamed out. The weaker solutions were made up as required by diluting the stock solutions for concentrations ranging down to 0.001 M. For the more dilute solutions a 0.001 M. stock solution was used and dilutions made from this. All dilutions were made at 25° using standard flasks and pipettes calibrated at 25° and all solutions were kept in Non-Sol bottles.

### Galvanometer

The galvanometer which was of the ballistic type, had the following characteristics: a sensitivity of 9090 megohms, a period of 21.4 seconds and a critical resistance of 35,000 ohms; the scale was 50 cm. from the galvanometer's mirror. The condenser was a standard mica instrument with steps of 0.001 microfarad to 0.5 microfarad and a total capacity of one microfarad. It was carefully calibrated in the Ernest Kempton laboratory, Department of Physics, Columbia University and found to be correct. For charging and discharging the condenser a key having double contacts and mounted on hard rubber was used. The several instruments, galvanometer, condenser, and key were set on rubber stoppers and all wires were run on insulators and all connections soldered. As a primary standard for e.m.f. a Weston standard cell was used; this had

<sup>1</sup> J. Amer. Chem. Soc. 31, 933 (1909).

<sup>2</sup> Z. Physik. Chem. 33, 611 (1900).

<sup>3</sup> loc. cit.

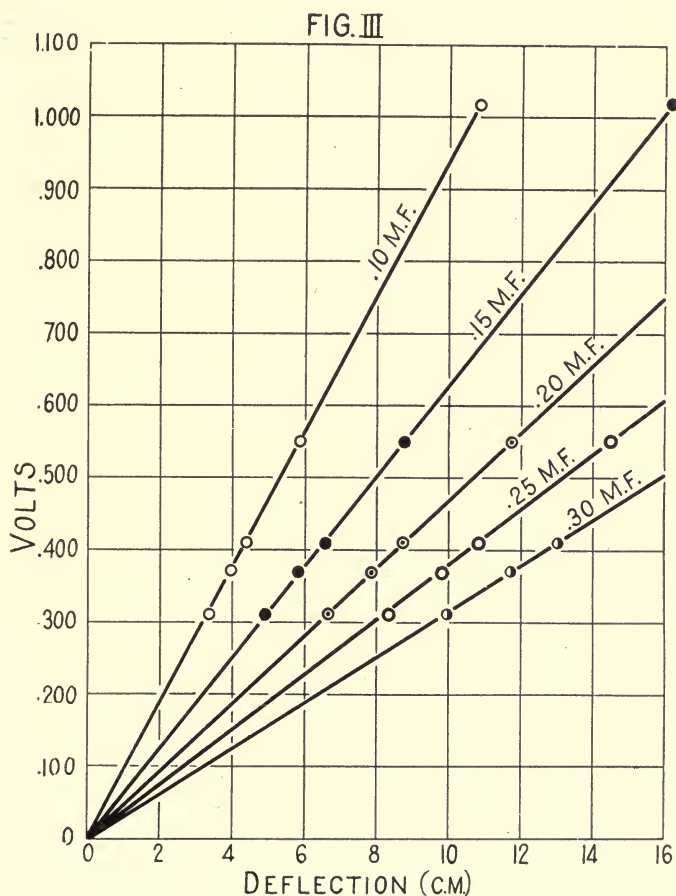
<sup>4</sup> The hydrochloric and sulfuric acids were standardized by titration against pure sodium carbonate using methyl-orange as indicator. Tenth molar sodium hydroxide was standardized against the hydrochloric acid and used for the standardization of the acetic acid, using phenolphthalein as indicator. The phosphoric was standardized gravimetrically using magnesia mixture as the precipitant and igniting the precipitate to magnesium pyrophosphate.



an e.m.f. of 1.0183 volts at 20° as was verified by checking against two other standard cells which had been certified by the U. S. Bureau of Standards.

### Calibration

The electromotive forces measured in this work ranged from 0.3 to 0.7 volts. The galvanometer was calibrated by taking various voltages<sup>1</sup> in this range and reading the deflection for the capacities, 0.10, 0.15, 0.20, 0.25, 0.30, of a microfarad. For each capacity a constant was obtained



<sup>1</sup>The voltages used for this calibration were obtained by using phosphate and citrate buffers according to Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore, 1920, page 68. The e.m.f. of these solutions were first measured on the potentiometer and then readings taken on the ballistic galvanometer.

by dividing the voltage by the deflection in scale divisions, graduated in centimeters. This is shown graphically in Fig. III, where voltage is plotted as the ordinate against deflection as the abscissa, a straight line resulting for each capacity. This procedure tends to minimize any errors due to irregularities in the scale or condenser.<sup>2</sup>

The calibration of the ballistic galvanometer could be checked whenever desired by using the standard Weston cell and an appropriate capacity. Observations taken throughout the course of the work showed that the total deflection for any given capacity and e.m.f. was constant, although the zero point of the galvanometer often shifted slightly,  $\pm 0.1$  cm., from reading to reading. As a further check, during routine measurements an e.m.f. was first determined by the ballistic galvanometer and then on the potentiometer, or by the standard cell using the ratio,  $E_{\text{std}} : E_x : \text{Def}_{\text{std}} : \text{Def}_x$ , where  $E_{\text{std}}$  is the e.m.f. of the standard cell,  $\text{Def}_{\text{std}}$  is the corresponding deflection on the ballistic galvanometer, and  $E_x$  and  $\text{Def}_x$  have a similar significance for the unknown cell. These methods gave checks within  $\pm 0.5$  milivolt.

It was found necessary to choose the capacity used in any given measurement so that the deflection read was between 10 and 15 cm. If the readings were more than 15 cm. the results are too low, as the observed readings are not then directly proportional to the tangent of the angle; if less than 10 cm. then the precision is too low. Under these restrictions the method is accurate to 0.5 milivolt as the deflection of the ballistic galvanometer can be read to  $\pm 0.2$  mm.

The apparatus was tested for electrical leaks as follows: The condenser was charged by means of the standard cell, this operation taking from one to two minutes; it was then immediately discharged through the ballistic galvanometer and the deflection noted; the condenser was again charged; disconnected from the standard cell by means of a switch, allowed to stand from five to ten minutes, and then discharged through the galvanometer and the deflection noted. On clear days the difference between these two deflections was about one centimeter for a deflection of 12 cm., so that on clear days the leakage for an immediate discharge of the condenser was negligible. On days, however, when the humidity was high the leakage was very rapid for if under these conditions the condenser was charged and allowed to stand only thirty seconds before discharging, the deflections would often be five or six centimeters different from that obtained from an immediate discharge of the condenser,

<sup>2</sup> In making a determination the solution whose concentration of hydrogen ion was to be determined was placed in the e.m.f. combination shown above, a certain capacity taken, the deflection read on the ballistic galvanometer and this reading multiplied by the constant for that capacity in order to give the observed e.m.f.

sometimes being greater, sometimes less. In consequence of the preceding observations the practice was always followed of making readings only on clear days; and it may be accepted with respect to the recorded results of this paper that the error due to the electrical leakage is in any case not greater than what corresponds to a deviation of  $\pm 0.1$  mm. in the galvanometer reading.

## EXPERIMENTAL RESULTS

The data obtained for the four different acids is given in the following tables, Nos. IV, V, VI, and VII. In each table the first column gives the molarity of the acid used; the second gives the observed electromotive force of the system measured (see page 8); the third gives the thermodynamic concentration of hydrogen ion as calculated by Nernst's

formula<sup>1</sup>, the fourth gives the ratio  $\frac{C_{H^+} \times 100}{C_{acid} \times \text{valence of anion}}$ , which in

other words is the percentage ionization based on the thermodynamic concentration of hydrogen ion. In the curves, Fig. IV, the values of column four are plotted as ordinates against the logarithm of the number of liters containing one mol of acid as abscissa. Each value is the mean of at least four determinations made on separate samples at different times, and for each value at least five readings of the galvanometer were taken over an interval of time from an hour to three hours or until they were constant.

<sup>1</sup> In making these calculations the value of  $K$  in Nernst's formula was taken as  $10^{-4.70}$  while the value of the contact potential between the saturated KCl salt bridge and the acid being employed was assumed to be zero. (For the validity of assumption just mentioned see the caption under Discussion entitled *Contact Potential*.)

An alternative method, identical in principle and effect with the foregoing, is to use the relationship  $\log C_{H^+}_x = \frac{0.2488 - E_{obs}}{0.059.11}$  which is obtained by re-arrange-

ment of the expression  $E_0 - E_{obs} = 0.05911 \log \frac{C_{H^+}_0}{C_{H^+}_x}$ , where  $E_0$  is the e.m.f. of

the system Hg—HgCl sat. KCl—0.1 M. HCl—H<sub>2</sub> (1 Atmos) Pt. for 25° and has the value of 0.3100 volt (cf. Fales and Mudge, loc. cit.),  $C_{H^+}_0$  is the concentration of hydrogen ion in 0.1 M. HCl at 25° and as determined by conductivity methods has the value 0.09204 M.,  $E_{obs}$  is the observed e.m.f. obtained by the use of combination (I).

TABLE IV  
Hydrochloric Acid

Conc. of acid	e.m.f. Obs.	$C_{H^+}$	$\frac{C_{H^+} \times 100}{C_{acid} \times 1}$
0.10 M	0.3100	$9.204 \times 10^{-2}$	92.0
0.01	.3657	$1.053 \times 10^{-2}$	105.3
0.005	.3820	$5.580 \times 10^{-3}$	111.6
0.001	.4225	$1.152 \times 10^{-3}$	115.2
0.0001	.4824	$1.117 \times 10^{-4}$	111.7
0.00005	.5011	$5.390 \times 10^{-5}$	107.8
0.00002	.5272	$1.950 \times 10^{-5}$	97.9
0.00001	.5521	$7.394 \times 10^{-6}$	73.9
0.000005	.5804	$2.455 \times 10^{-6}$	49.1
0.000001	.6376	$2.644 \times 10^{-7}$	26.4

TABLE V

## Acetic Acid

Conc. of acid	e.m.f. Obs.	$C_{H^+}$	$\frac{C_{H^+} \times 100}{C_{acid} \times 1}$
0.05 M	.4210	$1.221 \times 10^{-3}$	2.44
0.005	.4495	$4.24 \times 10^{-4}$	8.05
0.001	.4716	$1.701 \times 10^{-4}$	17.01
0.0002	.4979	$6.107 \times 10^{-5}$	30.5
0.0001	.5077	$4.169 \times 10^{-5}$	41.7
0.00005	.5219	$2.398 \times 10^{-5}$	47.95
0.00001	.5710	$3.540 \times 10^{-6}$	35.4
0.000005	.6104	$7.630 \times 10^{-7}$	15.3
0.000001	.6545	$1.370 \times 10^{-7}$	13.7

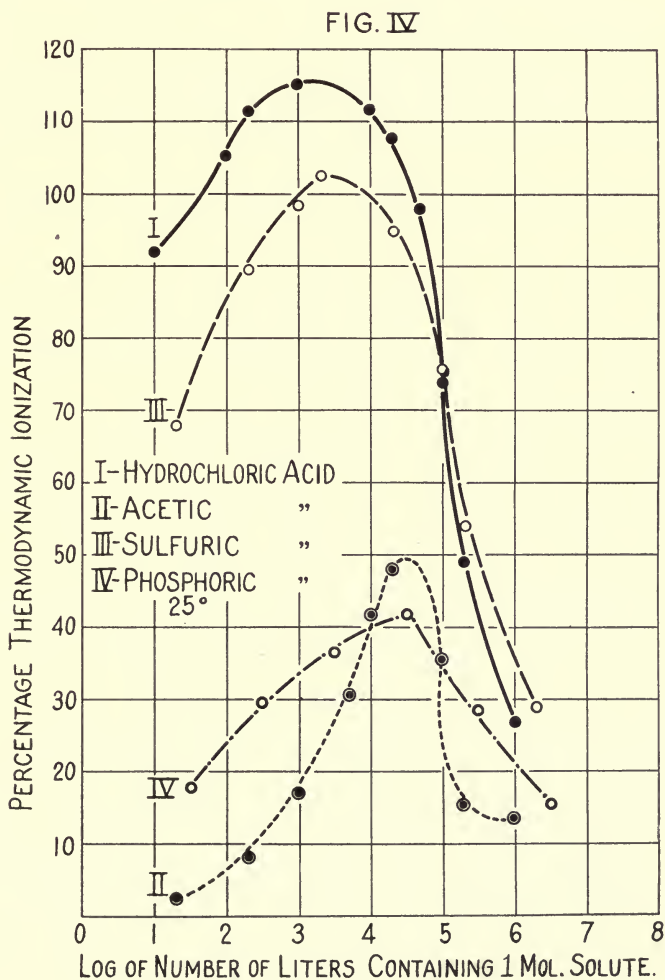
TABLE VI

## Sulfuric Acid

Conc. of acid	e.m.f. Obs.	$C_{H^+}$	$\frac{C_{H^+} \times 100}{C_{acid} \times 2}$
0.05 M	.3174	$6.802 \times 10^{-2}$	68.0
0.005	.3698	$8.974 \times 10^{-3}$	89.7
0.001	.3852	$4.926 \times 10^{-3}$	98.5
0.0005	.4255	$1.025 \times 10^{-3}$	102.5
0.00005	.4866	$9.484 \times 10^{-5}$	94.8
0.00001	.5096	$3.872 \times 10^{-5}$	75.7
0.000005	.5602	$5.394 \times 10^{-6}$	53.9
0.0000005	.6352	$2.904 \times 10^{-7}$	29.0

TABLE VII  
Phosphoric Acid

Conc. of acid	e.m.f. Obs.	$C_{H^+}$	$\frac{C_{H^+} \times 100}{C_{acid} \times 3}$
0.0333 M	.3582	$1.775 \times 10^{-2}$	17.75
0.00333	.3983	$2.957 \times 10^{-3}$	29.57
0.000333	.4517	$3.633 \times 10^{-4}$	36.33
0.0000333	.5077	$4.169 \times 10^{-5}$	41.69
0.00000333	.5766	$2.847 \times 10^{-6}$	28.47
0.00000033	.6516	$1.533 \times 10^{-7}$	15.33

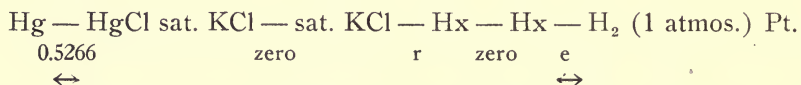


## DISCUSSION

In arriving at the degrees of ionization of the several acids under consideration, Tables IV to VII inclusive, three assumptions have tacitly been made and it consequently becomes necessary to consider in how far these assumptions affect the validity of the values which we have assigned. The three assumptions are: that the contact potential between the saturated potassium chloride salt bridge and the solution being measured is zero; that Nernst's formula for pole potential differences is valid; that the ionization of the respective acids is unaffected by the presence of any slight impurities that might have been present in the solution.

**Contact Potential**

As to the manner in which the value assigned to the contact potential affects the results, let us consider the particular e.m.f. system which was employed:



It can be seen that since we know only the observed value of the system and the value of the pole potential of the calomel cell,<sup>1</sup> we can not arrive at a value of the pole potential of the hydrogen electrode "e," until we know the value of the contact potential "r."

As a matter of direct experimentation it is not possible to determine "r," but from the indirect experimentation of Fales and Vosburgh<sup>2</sup> it would seem that the value of the contact potential between saturated potassium chloride and 1 M. hydrochloric acid and between saturated potassium chloride and 0.1 M. hydrochloric acid is zero<sup>3</sup>; and inferentially by a similar process of reasoning it likewise would seem that the contact potential between saturated potassium chloride and hydrochloric acid solutions of less concentration than 0.1 M. would be zero. If for

<sup>1</sup> The pole potential of the sat. KCl calomel electrode at 25° is equal to 0.5266 volt on the basis that the value of the normal calomel cell Hg—HgCl 1 M. KCl for 18° is 0.5600 volt as adopted by Ostwald, *Z. Physik. Chem.* **35**, 333 (1900), cf. Fales and Mudge (*loc. cit.*). Since the plus or minus sign attached to the value of a pole potential difference is simply to indicate the e.m.f. of the electrolyte against the electrode and leads to confusion when one is dealing with component potential differences of a combination, it is preferable to make use of arrows to indicate the direction in which the positive current tends to flow through the solution by virtue of the particular potential difference involved.

<sup>2</sup> *loc. cit.*

<sup>3</sup> This is also assumed by W. C. McC. Lewis, *loc. cit.*



such latter concentrations we approach the matter entirely on theoretical grounds by means of Planck's formula<sup>1</sup> for contact potential difference we can arrive at some estimate of limiting values of "r." To determine these limiting values, complete ionization was assumed for HCl of the following concentrations, and calculations<sup>2</sup> made accordingly with the following results, Table VIII.

TABLE VIII

Conc. HCl Mol per liter	0.01	0.001	0.0001	0.00001	0.000001
Value of "r" (volts)	0.0018	0.0018	0.0018	0.0018	0.0018

These potentials are directed so that the positive current tends to flow across the junction from the acid to the potassium chloride. If we assume the respective values of  $r = .0018$ , instead of  $r = \text{zero}$ , then the value which we would assign to the hydrogen pole potentials from the data of Tables IV to VII inclusive would be correspondingly greater, and thus larger values for the percentage thermodynamic ionization would result than the ones given in said tables.

To illustrate these considerations, the case of hydrochloric acid has been taken and Table IX gives in the first column the concentration of

TABLE IX

Conc. HCl	e.m.f. Obs.	$C_{H^+} \times 100$	$C_{H^+} \times 100$
		$\frac{C_{acid} \times 1}{(r=0)}$	$\frac{C_{acid} \times 1}{(r=.0018)}$
0.01 M	0.3657	105.3	112.9
.001	.4225	115.7	123.5
.0001	.4824	111.7	119.8
.00001	.5521	73.9	79.4
.000001	.6376	26.4	28.4

<sup>1</sup> Ann. Physik. 4, 581 (1890). The equation is:  $E = RT \log \xi$  where  $E$  is the contact potential difference in volts,  $R = 0.000198$ ,  $T$  is the absolute temperature and  $\xi$  is a transcendental function defined by the equation:

$$\xi U_2 - U_1 \log \frac{c_2}{c_1} - \log \xi \xi c_2 - c_1$$

$$\frac{V_2 - \xi V_1 \log \frac{c_2}{c_1} + \log \xi c_2 - \xi c_1}{}$$

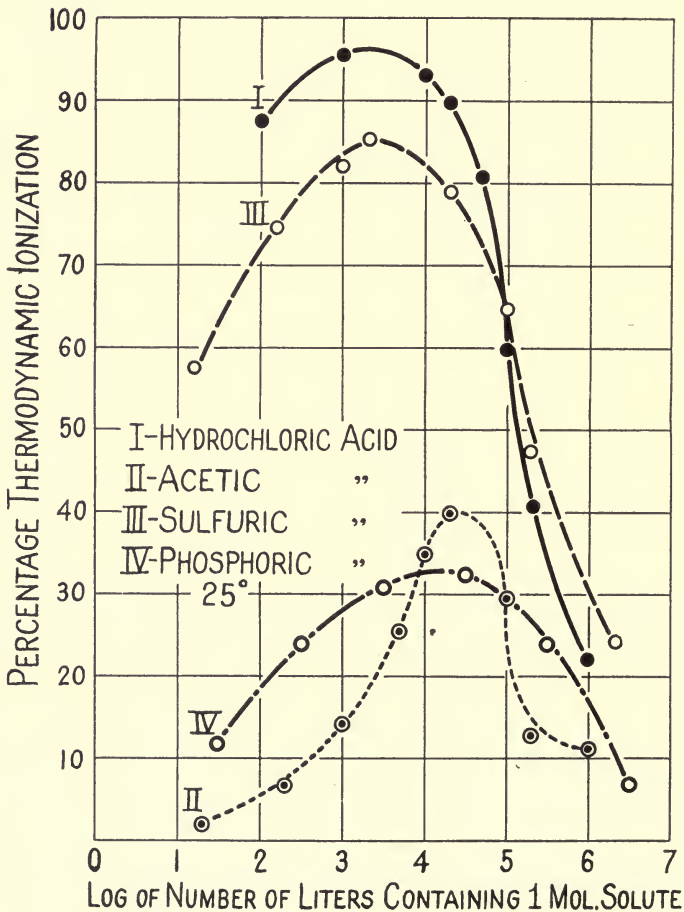
$U_1$  is the sum of the products of the mobilities of the positive ions in the dilute solution times their respective concentrations;  $V_1$  is the products of the negative ions in the dilute solution times their respective concentrations;  $c_1$  is the sum of the concentrations of the positive and negative ions in the dilute solution;  $U_2$ ,  $V_2$ , and  $c_2$  have a similar significance in regard to the concentrated solution.

<sup>2</sup> The method of calculation was that given by Fales and Vosburgh, loc. cit., and the data given there for the mobilities of the ions was taken for these calculations; the ionization of saturated potassium chloride (4.1 M.) at 25° was taken as 65%.

hydrochloric acid used, in the second the observed e.m.f. of the combination, in the third the percentage thermodynamic ionization for  $r = \text{zero}$ , and in the fourth the same for  $r = 0.0018 \text{ volt}$ .<sup>1</sup>

It will thus be seen that while the value we assign to the contact potential " $r$ " does affect the values we get for the thermodynamic degree of ionization, it will still be true for each separate set of values that the degree of ionization rises to a maximum and then falls off rapidly toward zero as the dilution increases. Compare Figs IV and V.

FIG. V



<sup>1</sup> The value of  $K$  in Nernst's formula was taken for these calculations as  $10^{-4.70}$ .

### Validity of Nernst Formula for Pole Potentials

Nernst<sup>1</sup> in deriving his general formula for the relationship between pole potential and ionic concentration, of which formula the one employed on page 8 of this article, namely  $e = .000198 T \log \frac{C_{H^+}}{K\sqrt{pH_2}}$

is a particular form, assumes that the gas laws are applicable to the ionized portion of electrolytes; or in other words that the *osmotic pressure of the ionized portion is proportional to its concentration*. Unfortunately we have no direct experimental method of testing this assumption although it is usually taken for granted that it applies to dilute solutions, say for ionic concentrations not greater than one-tenth molar. With this restriction as to the concentration of electrolyte it may be remarked that if the applicability of the gas laws is not true then the formula will have to be replaced by another of the type

$$e = .000198 T \log. \frac{C_{H^+}}{K\sqrt{pH_2}} + f(C_{H^+})$$

where the nature of the function  $f(C_{H^+})$  would have to be determined. If the gas laws do apply then the formula enables us to obtain ratios of values for the  $C_{H^+}$  as we pass from one concentration of acid to another, for letting  $e_1$  represent the pole potential corresponding to concentration of hydrogen ion  $c_1$ , and  $e_2$  and  $c_2$  have a similar significance with respect to another concentration we have

$$e_1 - e_2 = .000198 T \log. \frac{c_1}{c_2}$$

$$\text{or } \frac{c_1}{c_2} = 10 \frac{e_1 - e_2}{0.000198 T}$$

$$c_1 : c_2 :: 1 : 10 \frac{e_1 - e_2}{0.000198 T}$$

and so for any number of concentrations we would have

$$c_1 : c_2 : c_3 : \dots : c_n :: 1 : 10 \frac{e_1 - e_2}{0.000198 T} : 10 \frac{e_1 - e_3}{0.000198 T} : \dots : 10 \frac{e_1 - e_n}{0.000198 T}$$

To convert these ratios into absolute values it is only necessary to know the concentration of hydrogen ion corresponding to any one of the particular concentrations of acid. Before proceeding by this method, however, to get ratios of  $C_{H^+}$  as well as absolute values for various concen-

<sup>1</sup> Z. Physik Ch. 4, 129 (1889).

trations of hydrochloric acid it will be advantageous to construct a table, X, for hydrochloric acid at 25° giving the  $C_{H^+}$  as determined by the Arrhenius method of conductivity ratios:

TABLE X

Conc. HCl	0.1	0.01	0.001	0.0001	0.00001	0.000001
$C_{H^+}$ (Conductivity)	0.09204 <sup>1</sup>	0.09518 <sup>2</sup>	0.000991 <sup>3</sup>	.04993 <sup>4</sup>	0.0 <sub>5</sub> 996 <sup>4</sup>	0.0 <sub>6</sub> 999 <sup>4</sup>

Proceeding now by means of Nernst's formula to get values for the ratios of  $C_{H^+}$  after the manner just described, we obtain from the data of the first two columns of Table IV the following results for HCl at 25°.

TABLE XI

Conc. HCl	0.1	0.01	0.005	0.001	0.0001	0.00005
Ratios $_{H^+}$	1	.114	.0606	.0126	.00121	.000586
Conc. HCl		0.00002	0.00001		0.0000005	0.000001
Ratios $_{H^+}$		.000212	.0000803		.0000267	.0 <sub>3</sub> 287

Next taking as a reference value the figure 0.09204 for the concentration of hydrogen ion in 0.1 M. HCl at 25° (cf Table X) we get as values for the concentration of hydrogen ion in hydrochloric acid those which have already been given in the third column of Table IV. At this point it must be accentuated that the absolute values which are obtained for the  $C_{H^+}$  by the preceding method depend upon which concentration of hydrogen ion, evaluated by means of conductivity ratios, we select as reference standard. Thus if we take as our standard the figure 0.000991 for the concentration of hydrogen ion in 0.001 M. HCl (Table X) we get as values for the concentration of hydrogen ion for hydrochloric acid, those given in Table XII and which on an average differ by about 17% from those given in Table IV.

This discrepancy points to a certain inconsistency between Nernst's formula and the Arrhenius method of conductivity ratios, because if the

<sup>1</sup> Cf. Fales and Vosburgh.

<sup>2</sup> Calculated for 25° from the conductivity data of Noyes (loc. cit. p. 137) by use of the method of least squares and the equation  $\Lambda_{25^\circ} = a + b\alpha + c\alpha^2$ , where  $\alpha$  is the equivalent conductivity at 18°,  $\alpha_0$  is the temperature difference 25°—18°, and  $a$ ,  $b$  and  $c$  are constants for each case. For zero concentration HCl,  $a = 379$ ,  $b = 6.651$ ,  $c = -0.0111$ ; for 0.01 M. HCl,  $a = 368$ ,  $b = 5,270$ ,  $c = -0.0114$ .

<sup>3</sup> Kendall, J. Amer. Chem. Soc. 39, 7 (1917).

<sup>4</sup> Extrapolated values obtained by extrapolating the function  $\frac{1}{\Lambda} = \frac{1}{\Lambda_0} +$

TABLE XII

Conc. HCl	0.1	0.01	0.001	0.0001	0.00001	0.000001
C <sub>H<sup>+</sup></sub> (e.m.f.)	.0779	0.00876	0.000959	0.000093	0.0 <sub>0</sub> 599	0.0 <sub>0</sub> 22

two were strictly consistent it would make no difference in the absolute values which C<sub>H<sup>+</sup></sub> from Table X was taken as reference.

Another way of showing this inconsistency is to calculate the value of K in the formula  $e = .000198 T \log \frac{C_{H^+}}{K \sqrt{pH_2}}$ , using for C<sub>H<sup>+</sup></sub> the values given by conductivity ratios (Table X), if inconsistency exists, the values for K will not be constant.<sup>1</sup>

Performing the necessary calculations with the aid of data for  $e$  from Table IV we obtain the results given in Table XIII which plainly show the variation in the values of K, and particularly that the variation is the greatest in the regions where the Arrhenius method of conductivity ratios must resort to extrapolation.

TABLE XIII

Conc. HCl	C <sub>H<sup>+</sup></sub> Conductivity	$e$ volts	K
0.1 Normal	0.09204	0.2166	10 <sup>-4.70</sup>
0.01	.009518	.1609	10 <sup>-4.74</sup>
.001	.000991	.1031	10 <sup>-4.77</sup>
.0001	0.0000993*	.0422	10 <sup>-4.71</sup>
.00001	0.0 <sub>0</sub> 996*	-.0255	10 <sup>-4.57</sup>
.000001	0.0 <sub>0</sub> 999*	-.1090	10 <sup>-4.26</sup>

\* extrapolated values

Proceeding similarly for the cases of acetic, sulphuric, and phosphoric acids, we get by aid of data for  $e$  from Tables V, VI and VII the results given in Table XIV; wherein it is to be further pointed out that the K's are of quite a different order of magnitude from those of Table XIII.

<sup>1</sup>Lewis, J. A. C. S. 35, 24 (1913) discusses this point and says with reference to the form of Nernst's formula which he employed, namely,  $E = E_0 - \frac{RT}{F} \ln \frac{C_{H^+}}{\sqrt{pH_2}}$ ,

where E<sub>0</sub> corresponds to our K that "Unless the concentration of the hydrogen ion is exactly proportional to the activity, the value of E<sub>0</sub> calculated from this equation will not be constant, but in any case it will approach a constant value as the concentration approaches zero."

TABLE XIV

Conc. $\text{HC}_2\text{H}_3\text{O}_2$	Conductivity <sup>1</sup>	volts	K
0.05 Normal	0.000964	0.1056	$10_{-4.80}$
.005	.000311	.0771	$10_{-4.80}$
.001	.000127	.0550	$10_{-4.82}$
Conc. $\text{H}_2\text{SO}_4$			
0.1 Normal	0.107 <sup>2</sup>	0.2092	$10_{-4.51}$
.01	.0157	.1568	$10_{-4.46}$
.001	.00189	.1011	$10_{-4.43}$
Conc. $\text{H}_3\text{PO}_4$			
0.1 Normal	0.0731 <sup>2</sup>	0.1684	$10_{-3.99}$
.01	.0177	.1283	$10_{-3.92}$
.001	.00267	.0749	$10_{-3.84}$

There are several possibilities which suggest themselves in the way of explanations as to the inconsistency between the results arrived at by the Arrhenius method of conductivity ratios and the e.m.f. method of Nernst, and without wishing to favor any particular hypothesis or to draw any positive conclusions, the author would like to advance certain reflections which seem pertinent.

If the manifestations which are being respectively measured by the two methods belong to the same entity then it would appear probable that the e.m.f. method because of its basic premise that the gas laws apply to solutions should give results in close agreement with the conductivity method only when we are concerned with electrolytes which follow the law of mass action; further experimental work will be done to test this idea.

If the manifestations belong to different entities then the problem becomes more complicated. A possibility along this line of reasoning is that in aqueous solution of electrolytes we are dealing not with simple ions but with an equilibrium between water, hydrated and non-hydrated ions and that the conductivity method measures both kinds of ions while the e.m.f. method measures only the unhydrated. On this premise we would have for the equilibrium between the water and the two kinds of ions the relationship



and accordingly as we go toward infinite dilution the fraction of unhydrated ion would approach zero as a limit while the fraction of hydrated ion would approach unity. This idea seems to be in harmony with the

<sup>1</sup>Derived from data of Kendall, J. C. S. 101, 1283 (1912).

<sup>2</sup>Derived from data of Noyes for 25° Car. Pub. 63, 262 (1907).

<sup>3</sup>*n*, the number of mols of water entering into solvation would vary with dilution. For a resume of ideas on the hydration of ions, see Kendall, Proc. Nat. Acad. Sci., 7, 56 (1921) No. 2.



fact that the ionized fraction of an acid, as determined by e.m.f. approaches zero.

### Impurities

The impurities to be considered are those derived as follows: (a) from the original acids, (b) from the water, (c) from the solvent action of the solutions upon the glass of the containing stock bottles which were all of "Non-sol" glass, (d) from the solvent action of the solutions upon the glass of the hydrogen electrode vessels which were made of lime glass, (e) from contact of the solutions with the air during the opening of bottles and the operation of transferring from one vessel to another.

With respect to these several captions we have: (a) the impurities in the original acids would at most only constitute a minute fractional part of the acids and while the ratio of impurity to acid would remain constant as we passed from one dilution of acid to another, the absolute amount of impurity would be becoming infinitesimally small, consequently the effect of such impurities may be considered zero; (b) the water as freshly distilled and collected had an ammonia content of 0.5 mg.  $\text{NH}_3$  per liter, which, expressed in terms of molarity, is  $3 \times 10^{-8}$  mol per liter. The form in which this was present is not determinable, but from previous remarks<sup>1</sup> we will assume that it existed as ammonium carbonate in combination with carbon dioxide from (e). The effect of such a small concentration of  $(\text{NH}_4)_2\text{CO}_3$  would be negligible except perhaps for the very smallest concentrations of acids employed, say concentrations less than  $10^{-6}$  M. (c) Conductivity measurements showed no change in the specific conductivity of the solutions upon standing in the "Non-sol" bottles; this effect may be considered zero; (d) conductivity measurements showed an appreciable change in the specific conductivity of the solutions during the first sixty minute period following their introduction into the hydrogen-electrode vessel and then no further appreciable change; the e.m.f. measurements during the same period showed no change; it would seem reasonable, therefore, to regard this effect as negligible. (e) From the work of Kendall<sup>2</sup> it seems probable that all the solutions measured would have a  $\text{CO}_2$  content of about  $1.4 \times 10^{-5}$  M., which is that corresponding to the concentration of  $\text{CO}_2$  normally present in the air; the concentration of hydrogen ion due to this  $\text{CO}_2$  is not directly measureable because of the repressant action of the hydrogen ion from the particular acid under examination, namely hydrochloric, acetic, etc. In any event, it is not likely that the concentration of hydrogen ion contributed by the  $\text{CO}_2$  in the presence of any of the other acids

<sup>1</sup> See foot-note under caption headed "Preparation of Materials and Solutions."

<sup>2</sup> Above

could be greater than that contributed in their absence, and this latter concentration was found to be  $1.1 \times 10^{-7}$  M.; we may accordingly neglect the effect of the  $\text{CO}_2$  except perhaps for the smallest concentrations of acids measured, say  $1 \times 10^{-6}$  M. or less, and even here the corrections would not materially affect the order of results found without applying any correction.

### Conclusions

I. Evidence has been presented to show that the degree of ionization of the acids hydrochloric, acetic, sulphuric and phosphoric as determined by measurements of their hydrogen ion concentrations by the electromotive force method of Nernst goes through a maximum and approaches zero as the dilution is indefinitely increased.

II. Certain aspects of the theory underlying the two principal methods now in use for determining the degree of ionization of electrolytes, that of conductivity ratios and that of electromotive force measurements, are discussed in the light of the experimental facts advanced.

## VITA

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